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Mechanism for Oxidation of Phenylacetylenes with Peroxymonophosphoric Acid. Oxirene as an Intermediate Inconvertible to Ketocarbene[1]

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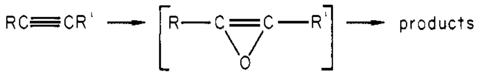
Abstract: Peroxymonophosphoric acid (H_3PO_5) is shown to be an effective oxidant for acetylenes. Phenylacetylenes, PhC≡CR (R = Ph, H, and Me), afford diketones (PhCOCOR), benzoic acid, and rearranged acids ($PhRCHCO_2H$). The relative migratory aptitude is in the order of H ≫ Me > Ph, which is in agreement with the order of H ≫ Ph ~ Me for the Wolff rearrangement of α-diazo ketones. However, the oxidation of acetylenes in MeOH–MeCN does not yield α-methoxy ketones, while the decomposition of α-diazo ketones affords significant amounts of the O–H inserted products. GLC or GC–MS analysis shows that the acetylene oxidation affords no detectable amount of products derived from ketocarbene. Oxirene intermediate, formed by the electrophilic oxidation of acetylenes, may be oxidized to diketones or may rearrange without involvement of ketocarbenes. Hence, ketocarbene–ketocarbene interconversions should proceed via an intermediate (e.g., **16**) other than oxirene-like ones.

Although peroxymonophosphoric acid (H_3PO_5)[2,3] seems to be a strong and effective oxidant, only a few reports appeared on organic oxidations.[4] We have recently shown that H_3PO_5 is much more effective than peroxyacetic or peroxybenzoic acid for the oxidation of acetophenones,[5a] benzaldehydes,[5b] amines,[6] stilbene,[7] tetrahydrofuran,[8] and phenols.[9]

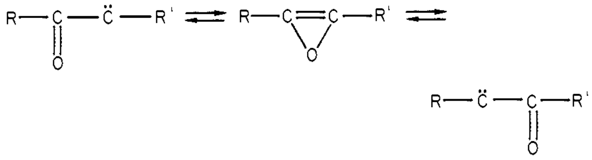
By analogy with the epoxidation of olefins, oxirene intermediates have been assumed for the oxidation of acetylenes (eq 1).[10] The



(1)

Wolff rearrangement of α-ketocarbenes to ketenes has been also explained by an oxirene intervention,[11-14] and the ketocarbene–oxirene equilibria (eq 2) are suggested in the decomposition of labeled α-diazo ketones.[12,13]

Ketocarbene–ketocarbene interconversion has been proved for acyclic α-diazo ketones,[14] but the interconversion is sometimes excluded for cyclic ones[15] and in catalytic decompositions.[13d,14]



(2)

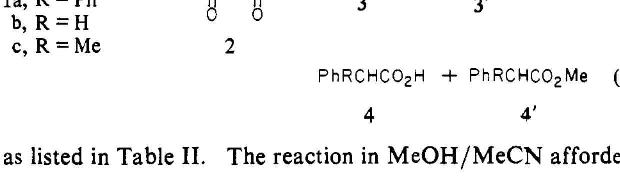
Since the peroxy acid oxidation of acetylenes affords rearranged products, an intervention of ketocarbene is conceivable. Hence the oxidation may proceed via oxirene,[10] ketocarbene,[12d] or an equilibrated mixture of oxirene and ketocarbene.[16] We report here the results of our mechanistic study on the H_3PO_5 oxidation of phenylacetylenes. The photochemical and thermal decomposition of the corresponding α-diazo ketones was also carried out for comparison. The trapping experiment with MeOH implied that ketocarbenes are not involved in the oxidation of acetylenes, thus denying the interconversion between oxirene and ketocarbene.

Results and Discussion

Oxidation of Acetylenes. Diphenylacetylene (**1a**), phenylacetylene (**1b**), and phenylmethylacetylene (**1c**) were oxidized with H_3PO_5 at room temperature in acetonitrile or acetonitrile/methanol (1:1 v/v). The rates were followed iodometrically, and the products were identified by GC–MS spectra together with NMR and IR in comparison with authentic samples, yields being determined by GLC.

The reaction of the acetylenes with H_3PO_5 obeyed second-order kinetics, i.e., first order in each reactant. In Table I are listed the rate constants for the three acetylenes together with those with peracetic acid and for the corresponding olefins. The resulting relative order of **1c** ≫ **1b** > **1a** for the phenylacetylenes suggests an electrophilic attack of H_3PO_5 on acetylene as reported previously for the oxidation with peroxy acid.[10e] The oxidation with H_3PO_5 is more than 10-fold faster than with peracetic acid, and the corresponding olefins were ca. 10-fold more reactive than acetylenes.

The oxidation products were diketones (**2**), benzoic acid (**3**), methyl benzoate (**3'**), and rearranged products **4** and **4'** (eq 3),



$$\mathrm{PhC{\equiv}CR} \xrightarrow{H_3PO_5} \mathrm{PhC(=O)-C(=O)R} + \mathrm{PhCO_2H} + \mathrm{PhCO_2Me} + \mathrm{PhRCHCO_2H} + \mathrm{PhRCHCO_2Me} \quad (3)$$

1a, R = Ph
b, R = H
c, R = Me

2, 3, 3', 4, 4'

as listed in Table II. The reaction in MeOH/MeCN afforded

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[1] Contribution No. 294.

[2] (a) Toennies, G. *J. Am. Chem. Soc.* **1937**, *59*, 555. (b) Chulski, T. *Diss. Abstr.* **1954**, *14*, 1904. (c) Schenk, P. W.; Dommain, K. *Z. Anorg. Allgem. Chem.* **1963**, *326*, 139. (d) Mamantov, G.; Burns, J. H.; Hall, J. R., Lake, D. B. *Inorg. Chem.* **1964**, *3*, 1043.

[3] (a) Goh, S. H.; Heslop, R. B.; Lethbridge, J. W. *J. Chem. Soc.* **1966**, 1302. (b) Battaglia, C. J.; Edwards, J. O. *Inorg. Chem.* **1965**, *4*, 552.

[4] Boyland, E.; Manso, D. *J. Chem. Soc.* **1957**, 4689.

[5] (a) Ogata, Y.; Tomizawa, K.; Ikeda, T. *J. Org. Chem.* **1978**, *43*, 2417. (b) Ogata, Y.; Sawaki, Y.; Tsukamoto, Y. *Bull. Chem. Soc. Jpn.* **1981**, *55*, 2061.

[6] Ogata, Y.; Tomizawa, K.; Morikawa, T. *J. Org. Chem.* **1979**, *44*, 352.

[7] Ogata, Y.; Tomizawa, K.; Ikeda, T. *J. Org. Chem.* **1979**, *44*, 2362.

[8] Ogata, Y.; Tomizawa, K.; Ikeda, T. *J. Org. Chem.* **1980**, *45*, 1320.

[9] Ogata, Y.; Sawaki, Y.; Tomizawa, K.; Ohno, T. *Tetrahedron* **1981**, *37*, 1485.

[10] (a) McDonald, R. N.; Schwab, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 4866. (b) Stille, J. K.; Whitehurst, D. D. *Ibid.* **1964**, *86*, 4871. (c) Schlubach, H.; Franzen, V. *Liebigs Ann. Chem.* **1952**, *577*, 60. (d) Ibne-Rasa, K. M.; Pater, R. H.; Ciabattoni, J.; Edwards, J. O. *J. Am. Chem. Soc.* **1973**, *95*, 7894. (e) Ogata, Y.; Sawaki, Y. Inoue, H. *J. Org. Chem.* **1973**, *38*, 1044.

[11] (a) Arnold, R. T.; Huggett, C.; Taylor, T. I. *J. Am. Chem. Soc.* **1942**, *64*, 3043. (b) Franzen, V. *Liebigs Ann. Chem.* **1958**, *614*, 31.

[12] (a) Csizmadia, I. G.; Font, J.; Strausz, O. P. *J. Am. Chem. Soc.* **1968**, *90*, 7360. (b) Thornton, D. E.; Gosavi, R. K.; Strausz, O. P. *Ibid.* **1970**, *92*, 1768. (c) Frater, G.; Strausz, O. P. *Ibid.* **1970**, *92*, 6654. (d) Fenwick, J.; Frater, G.; Ogi, K.; Strausz, O. P. *Ibid.* **1973**, *95*, 124.

[13] (a) Zeller, K.-P.; Mejer, H.; Kolshorn, H.; Müller, E. *Chem. Ber.* **1972**, *105*, 1875. (b) Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 781. (c) Zeller, K.-P. *Tetrahedron Lett.* **1977**, 707. (d) Timm, U.; Zeller, K.-P.; Meier, H. *Chem. Ber.* **1978**, *111*, 1549. (e) Zeller, K.-P. *Ibid.* **1979**, *112*, 678.

[14] (a) Matlin, S. A.; Sammes, P. G. *J. Chem. Soc., Chem. Commun.* **1972**, 11; *J. Chem. Soc., Perkin Trans. 1* **1972**, 2623. (b) Tomioka, H.; Okuno, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7123.

[15] (a) Zeller, K.-P. *Chem. Ber.* **1975**, *108*, 3566. (b) Timm, U.; Zeller, K.-P.; Meier, H. *Tetrahedron* **1977**, *33*, 453. (c) Majerski, Z.; Redvanly, C. S. *J. Chem. Soc., Chem. Commun.* **1972**, 694.

[16] (a) Ciabattoni, J.; Campbell, R. A.; Renner, C. A.; Concannon, P. W. *J. Am. Chem. Soc.* **1970**, *92*, 3826. (b) Concannon, P. W.; Ciabattoni, J. *Ibid.* **1973**, *95*, 3284. (c) Franzen, V. *Liebigs Ann. Chem.* **1957**, *602*, 199.

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Table I. Rate Constants for the Oxidation of Phenylacetylenes and Olefins with H_3PO_5 and $MeCO_3H$ in MeCN at 30 °C[a]

substrate	$k \times 10^4$, M^{-1} s^{-1}	
	H_3PO_5	$MeCO_3H$
PhC≡CPh (1a)	2.3	0.10
trans-PhCH=CHPh	35	
PhC≡CH (1b)	2.9	0.11
$PhCH{=}CH_2$	48	
PhC≡CMe (1c)	17	0.31

[a] Reaction with 0.20 M acetylenes or olefins with 0.020 M peracid.

Table II. Products from the Oxidation of Acetylenes with H_3PO_5

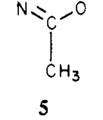
acetylene	reaction time	solvent	product yields, %[a]				
			2	3	3'	4	4'
1a	4 h	MeCN	48	19		1.1	
	1 day	MeOH/MeCN[b]	15	40	64	0	6.5
1b	4 h	MeCN	0	36		17	
	1 day	MeOH/MeCN	0	20	15	0	28
1c	2 h	MeCN	20	39		1.7	
	1 day	MeOH/MeCN	24	21	21	0	9.3

[a] Yields are based on acetylenes consumed for the reaction with 0.16 M acetylene and 0.48 M H_3PO_5 at room temperature. Conversion of H_3PO_5 were 70–90% for each run. [b] MeOH–MeCN (1:1 v/v).

exclusively methyl esters **4'**. The formation of acids **4** in MeCN is explicable by ketene and contaminated water. In the case of **1b**, phenylglyoxal (**2b**) could not be detected, probably because **2b** is easily oxidized to benzoic acid. Although intermediary diphenylketene was reported to be oxidized to benzophenone in the peroxy acid oxidation of **1a**,[10b] benzophenone (from **1a**), acetophenone (from **1c**), or their further oxidized products were not detected in the present H_3PO_5 oxidation. This means that the reaction of ketene intermediates with methanol or water is much faster than their further oxidation to ketones.

The relative yields for the rearranged products **4** and **4'** showed a migratory aptitude of H ≫ Me > Ph (Table II), which agrees with the reported one of H ≫ Ph ~ Me for the Wolff rearrangement from α-diazo ketones.[17] Similar products may be obtained from phenylacetylenes by refluxing with trifluoroperoxyacetic acid in dichloromethane,[10a] e.g., 76% of **2a** and 17% of **3** from **1a**, 38% of **4b** and 25% of **3** from **1b**. But the oxidation with other peroxy acids is very slow and not practical. In contrast, H_3PO_5 is a good oxidant for acetylenes effective at room temperature.

Other compounds (e.g., **5** and **6**), which are conceivable if intermediary ketocarbene were involved, could not be detected, i.e., oxazole **5**, a product from ketocarbene and acetonitrile,[18] O–H insertion products **6** from ketocarbene and methanol or water, and acetophenone as a product from **1b** via the H abstraction of ketocarbene.[19] None of these compounds could be detected from the present H_3PO_5 oxidation.



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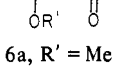
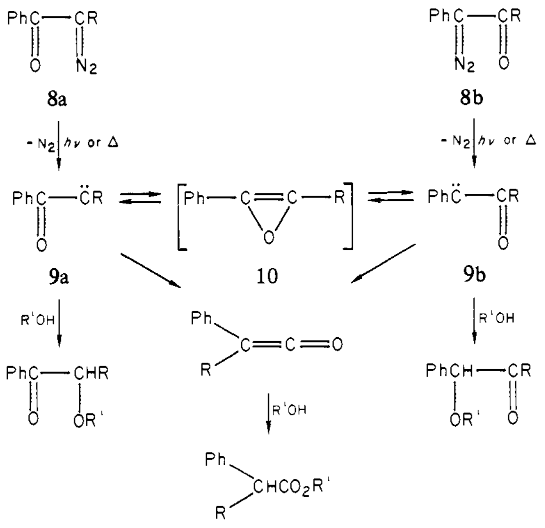
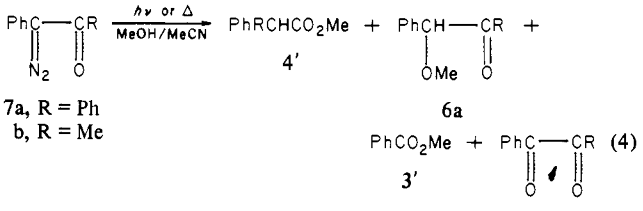


6a, R' = Me
b, R' = H

Decomposition of α-Diazo Ketones. In order to compare with the results for H_3PO_5 oxidation of acetylenes, were examined the photolysis and thermolysis of corresponding α-diazo ketones, viz., azibenzil (**7a**) for **1a** and phenylacetyldiazomethane (**7b**) for **1c**. Photochemical and thermal decompositions of the α-diazo ketones in MeOH/MeCN gave the same product but of different ratios as shown in Table III. The major products were ester **4'** via the Wolff rearrangement, α-methoxy ketone **6a**, and methyl benzoate **3'** (eq 4).

Scheme I





$$\mathrm{PhC({=}N_2){-}C({=}O)R} \xrightarrow[\mathrm{MeOH/MeCN}]{h\nu \text{ or } \Delta} \underset{\mathbf{4'}}{\mathrm{PhRCHCO_2Me}} + \underset{\mathbf{6a}}{\mathrm{PhCH(OMe){-}C({=}O)R}} + \underset{\mathbf{3'}}{\mathrm{PhCO_2Me}} + \underset{\mathbf{2}}{\mathrm{PhC({=}O){-}C({=}O)R}} \quad (4)$$

7a, R = Ph
b, R = Me

It is generally accepted that the Wolff rearrangement proceeds via ketocarbenes,[20] though someone assumed a concerted migration from α-diazo ketone.[21] For the present decomposition in MeOH/MeCN, the O–H insertion product **6a** is surely formed via trapping ketocarbenes with methanol. On irradiation at >400 nm, the product ratios changed significantly with irradiation times and the presence of oxygen (Table III). The rearranged product **4'** was stable under the irradiation conditions, but α-methoxy ketone **6a** was photodecomposed significantly in the presence of oxygen. The product–time curves indicate that **6a** is photooxidized to methyl benzoate as recently reported by us.[22] Thence the

$$\mathbf{6a} \xrightarrow{h\nu} \mathrm{Ph\dot{C}HOMe} \xrightarrow{O_2} \rightarrow \mathrm{PhCO_2Me}$$

combined yield of **6a** and **3'** represents the true yield of **6a** as an O–H insertion product. The ratios of (**6a** + **3'**)/**4'** at the initial stage (i.e., 10-min irradiation) show that the O–H insertion decreases with increasing temperature (Table III), suggesting that unimolecular Wolff rearrangement of ketocarbene has a higher activation energy compared with its bimolecular O–H insertion to methanol. In fact, the ratio for photolysis is practically the same as that for thermolysis at the same temperature (80 °C). Similar ratios of products at the final stages were reported for the thermolysis of **8a**[23] and the photolysis of **8b** in methanol.[14b]

The formation of a small amount of benzil in the photolysis of azibenzil might be explicable either by the dimerization of benzoyl radical $\mathrm{Ph\dot{C}{=}O}$[24] or by the direct reaction of ketocarbene with oxygen.[25] But another mechanism via singlet oxygen[26] seems

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(17) Huisgen, R.; Binsch, G.; Chosez, L. *Chem. Ber.* **1964**, *97*, 2628.
(18) Padwa, A.; Layton, R. *Tetrahedron Lett.* **1965**, 2167.
(19) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.
(20) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; p 476.
(21) Kaplan, F.; Meloy, G. K. *J. Am. Chem. Soc.* **1966**, *88*, 950.
(22) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2049.
(23) Schroeter, G. *Chem. Ber.* **1909**, *42*, 3356.
(24) Lewis, F. D.; Lauterbach, R. T.; Heine, H.-G.; Hartmann, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519.

Table III. Photochemical and Thermal Reactions of α-Diazo Ketones in MeOH-MeCN (1:1 v/v)[a]

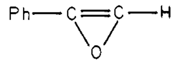
α-diazo ketone	reaction conditions[b]	products, %[c]				
		4′	6a	3′	2	(6a + 3′)/4′
7a	photolysis,[d] air, 10 min	11	21	2	3	2.1
	N_2, 10 min	10	30	0.3		3.0
	air, 120 min	49	2	27	6	0.59
	N_2, 120 min	64	30	4		0.53
	air, 80 °C, 10 min	60	4	19	6	0.38
	thermolysis reflux, 80 °C, 420 min	73	25	1		0.36
7b	photolysis,[d] air, 10 min	9	14	0.5		1.6
	air, 240 min	31	8.5	41		1.6
	N_2, 240 min	33	33	1		1.03
	thermolysis reflux, 80 °C, 420 min	33	36	0.4		1.10

[a] Reaction with 0.04 M 7 for photolysis and 0.2 M for thermolysis. [b] Reaction at room temperature (~25 °C), unless noted otherwise. [c] Yields were determined by GLC and based on the α-diazo ketone charged. [d] Irradiated at >400 nm.

to be more probable since the addition of Methylene Blue doubled or tripled the yield of benzil.

Mechanism. It is generally accepted that the Wolff rearrangements proceed via ketocarbene,[20] ketocarbene–ketocarbene interconversions being proved (Scheme I).[12-14] But the interconversion between ketocarbene and oxirene has never been proved experimentally.

Several theoretical calculations have been done on oxirene and ketocarbene. Ketocarbene is calculated to be more stable than oxirene according to EHMO[27] and ab initio SCF-MO methods,[28,29] while the reverse results are reported by the MINDO/3 method.[30] These calculations were carried out mostly for the parent ketocarbene and oxirene, i.e., R = R′ = H in eq 2. For the examination of substituent effect on their energies, we calculated the energies of oxirene **11** and ketocarbene **12** and **13** as conceivable intermediates for the present oxidation. Their energies were calculated by the semiempirical MINDO/3 method[31] according to the optimized geometry for parent compounds.[28a] Ketocarbene **12** is calculated to be more stable by 14 kcal/mol than its isomer **13**,[32] whereas oxirene **11** is more stable by 4 kcal/mol than ketocarbene **12** in agreement with Dewar's results on the parent compounds.[30] Thus, ab initio and MINDO/3 methods gave reverse results, but the energy differences are small and not conclusive. Hence the answer is open to experimental examinations.



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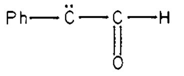

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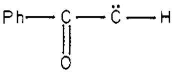

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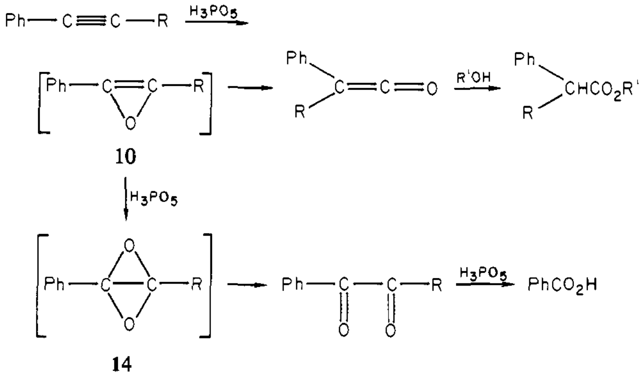
It is reasonable to assume that acetylenes are attacked by electrophilic peroxidic oxygen to form oxirenes in analogy to epoxidation of olefins.[10] The open question here is whether ketocarbenes are intermediates or not involved. Major products from the H_3PO_5 oxidation of phenylacetylenes are diketones and the rearranged acids **4** and **4′**. In contrast, the major products from α-diazo ketones in MeOH–MeCN are rearranged acids and α-methoxy ketones **6a**, both of which are derived from a ketocarbene intermediate (Scheme I). In the H_3PO_5 oxidation of phenylacetylene, however, we could not detect **6a** even with sensitive GC–MS technique. The control reaction of benzoin methyl ether (**6a**, R = Ph) and 1-methoxy-1-phenyl-2-propanone (**6a**, R = Me) with H_3PO_5 for 1 day under the same conditions resulted in the recovery of 40–50% of the α-methoxy ketones; hence α-methoxy ketones are not formed in the H_3PO_5 oxidation of acetylenes. Similarly, no α-methoxy ketone was detected in the peracetic acid oxidation of phenylacetylenes at 80 °C. Since ketocarbenes are known to be trapped efficiently by alcohols[14b,23] at almost diffusion-controlled rate,[33] ketocarbenes are not involved in the oxidation of acetylenes. Although ketocarbene–ketocarbene interconversions are often written as involving an oxirene intermediate (Scheme I), it may be concluded that oxirenes and ketocarbenes are inconvertible to each other. Then a reasonable mechanism for the acetylene oxidation would be formulated as Scheme II, not involving ketocarbene. That is, oxirene **10** is oxidized to diketone or rearranges to ketene affording rearranged acid or its ester. The competition between the oxidation and rearrangement of **10** is reflected in the decreasing yields of rearranged product **4′** with increasing concentration of H_3PO_5; i.e., the ratio **4′**/(**2** + **3**/2) is 0.21, 0.17, and 0.097 for the oxidation of **1a** with 0.048, 0.096, and 0.48 M H_3PO_5, respectively, in MeOH/MeCN.

Scheme II



The oxidation of oxirene **10** is probably facile, since its highly strained energy[34] is released in dioxirane **14** and vinyl ethers are susceptible to electrophilic attacks.[35] The rearrangement of oxirene **10** to ketene is probably concerted, the driving force being again the release of strain in **10**. The rearrangement is accelerated by a hydrogen bonding to oxygen in oxirene (**15**), since the yields

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(25) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

(26) (a) Higley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 3330. (b) Ando, W.; Miyazaki, H.; Kohmoto, S. *Tetrahedron Lett.* **1979**, 1317. (c) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832.

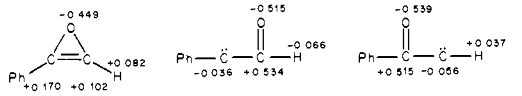
(27) Csizmadia, I. G.; Gunning, H. E.; Gosavi, R. K.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 133.

(28) (a) Strausz, O. P.; Gosavi, R. K.; Denes, A. S.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1976**, *98*, 4784. (b) Strausz, O. P.; Gosavi, R. K.; Gunning, H. E. *J. Chem. Phys.* **1977**, *67*, 3057.

(29) Tanaka, K.; Yoshimine, M. *J. Am. Chem. Soc.* **1980**, *102*, 7655.

(30) Dewar, M. J. S.; Ramsden, C. A. *J. Chem. Soc., Chem. Commun.* **1973**, 688.

(31) Planar structures were assumed and calculated. Charge distributions calculated for **11**, **12**, and **13** are as follows:

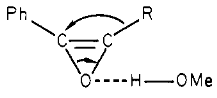


(32) This large energy difference agrees with the exclusive formation of **6a** by trapping **12** with methanol solvent.

(33) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(34) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

(35) Plesnicar, B. "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, p 211.



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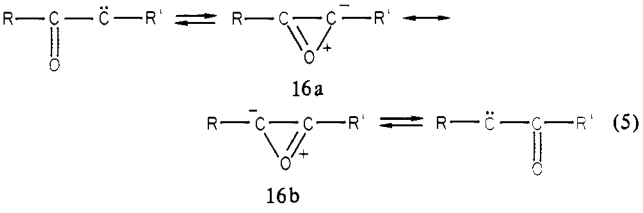
of rearranged products increased by a factor of 2–6 on changing solvent from acetonitrile to methanol. The rearrangement via oxirene seems to explain the difference in product ratios between the peracid oxidation of cyclic acetylenes and the decomposition of corresponding α-diazo ketones.[16b]

In spite of low energy barriers calculated for the isomerization of oxirene to ketocarbene (i.e., 2[29] and 7 kcal/mol[28a]), the present experimental results deny the estimation. Hence, experimentally established ketocarbene–ketocarbene interconversion should proceed without intervention of oxirene. A tentative scheme for the interconversion is oxygen atom migration via **16** (eq 5). The



intermediate **16** is different from oxirene **10** in that **16** possesses a C=O double bond. Similar dipolar species but of acyclic structure are often written for the intermolecular reactions of carbenes with ethers or carbonyls.[36] The calculated charge on the methylene carbon atom in ketocarbene **12** or **13** is very small or nearly neutral,[31] and hence the intramolecular ylide formation as a typical carbene (eq 5) may be supposed to be facile, resulting in the establishment of fast ketocarbene–ketocarbene equilibrium.

Experimental Section

IR and NMR spectra were recorded on a Perkin-Elmer 337 and a Hitachi R-24 spectrometer, respectively. GLC analysis was carried out by a Yanagimoto G180 gas chromatograph with diphenyl as an internal standard and two columns: PEG 20M, 10% on Chromosorb WAW, 2.5 mm × 1 m; and Silicone OV 17, 5% on Shimalite W, 2.5 mm × 1 m. GC–MS spectra were recorded on a JEOL JMS D300 mass spectrometer.

Materials. Peroxymonophosphoric acid was prepared from phosphorus pentoxide and 90% hydrogen peroxide in acetonitrile.[2a] The peracid is surely H_3PO_5 on the basis of the fact that its pK_a values, titrated[6] or determined kinetically from the oxidation of Me_2SO,[5b] agreed approximately with the reported ones.[3] That there was no contamination by H_2O_2 was confirmed by titration with $KMnO_4$. Diphenylacetylene (**1a**) and phenylacetylene (**1b**) were prepared from *trans*-stilbene[37] and styrene,[38] respectively, according to reported methods. Phenylmethylacetylene (**1c**) was prepared by the methylation of phenylacetylene with dimethyl sulfate.[39] Azibenzil (**7a**) was prepared from benzil by the treatment with hydrazine hydrate and mercuric oxide.[40] Phenylacetyldiazomethane (**7b**) was synthesized by the treatment of benzyl methyl ketone with tosyl azide.[41] 1-Methoxy-1-phenyl-2-propanone (**6a**, R = Me) was prepared by the boron trifluoride catalyzed reaction of phenylacetyldiazomethane with methanol.[42]

Typical Procedure for the Oxidation of Acetylenes. To a solution of 0.178 g (1.0 mmol) of **1a** in 4.8 mL of MeCN was added 1.5 mL (3.0 mmol) of 2 M H_3PO_5 in MeCN. After stirring for 4 h at room temperature, the reaction mixture was diluted with water, extracted with ether, and dried. After condensation, products were determined by GLC and/or GC–MS analysis in comparison with authentic samples. Carboxylic acids were analyzed after the methylation with diazomethane. Benzil was isolated by ether extraction after neutralization with $NaHCO_3$, and its GC–MS, IR, and NMR spectra were identical with those of an authentic sample.

The oxidation rate was determined iodometrically following the disappearance of H_3PO_5 under pseudo-first-order conditions with 0.20 M (excess) acetylene and 0.02 M H_3PO_5. The resulting second-order rate constants are listed in Table I.

Decomposition of α-Diazo Ketones. Photolysis of α-diazo ketones was conducted with a medium-pressure Hg lamp by irradiating at >400 nm through an aqueous 5% $NaNO_2$ filter solution. Typically a solution of 0.0888 g (0.4 mmol) of azibenzil in 10 mL of MeOH–MeCN (1:1 v/v) was irradiated. Thermolyses of α-diazo ketones were conducted by refluxing at 80 °C; e.g., a solution of 0.444 g (2.0 mmol) of azibenzil in 10 mL of MeOH–MeCN (1:1) was refluxed. The products were identified and determined by comparing their GLC or GC–MS spectra with those of authentic samples.

H_3PO_5 Oxidation of α-Methoxy Ketones. To a solution of 0.113 g (0.5 mmol) of benzoin methyl ether (**6a**, R = Ph) in 2.5 mL of methanol was added 0.75 mL (1.5 mmol) of 2 M H_3PO_5 in 1.8 mL of acetonitrile. After stirring for 1 day at room temperature, the reaction mixture was analyzed by GLC and GC–MS. Products identified were benzoic acid (19%) and methyl benzoate (19%) together with 46% of recovered benzoin methyl ether, *m/e* being 226, 121, and 105 by GC–MS.

The similar oxidation of 1-methoxy-1-phenyl-2-propanone (**6a**, R = Me) afforded methyl benzoate (10%) and benzaldehyde (25%), 40% of starting material (*m/e* 164, 121, and 43) being recovered.

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Registry No. 1a, 501-65-5; **1b**, 536-74-3; **1c**, 673-32-5; **6a** (R = Me), 7624-24-0; **6a** (R = Ph), 19190-53-5; **7a**, 3469-17-8; **7b**, 3893-35-4; H_3PO_5, 13598-52-2; *trans*-PhCH=CHPh, 103-30-0; PhCH=CH_2, 100-42-5.

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(36) Reference 20, p 411.

(37) Smith, L. I.; Falkof, M. M. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, p 350.

(38) Fiesselman, H.; Sasse, K. *Chem. Ber.* **1956**, *89*, 1775.

(39) Bergmann, E.; Bondi, A. *Chem. Ber.* **1933**, *66*, 278.

(40) Nenitzescu, C. D.; Solomonica, E. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. 2, p 496.

(41) Regitz, M. *Chem. Ber.* **1965**, *98*, 1210.

(42) Newman, M. S.; Beal, P. F., III. *J. Am. Chem. Soc.* **1950**, *72*, 5161.